Study of Enhancements in Nitric Acid Above the Primary Peak Using Aura-MLS, ACE-FTS and SLIMCAT

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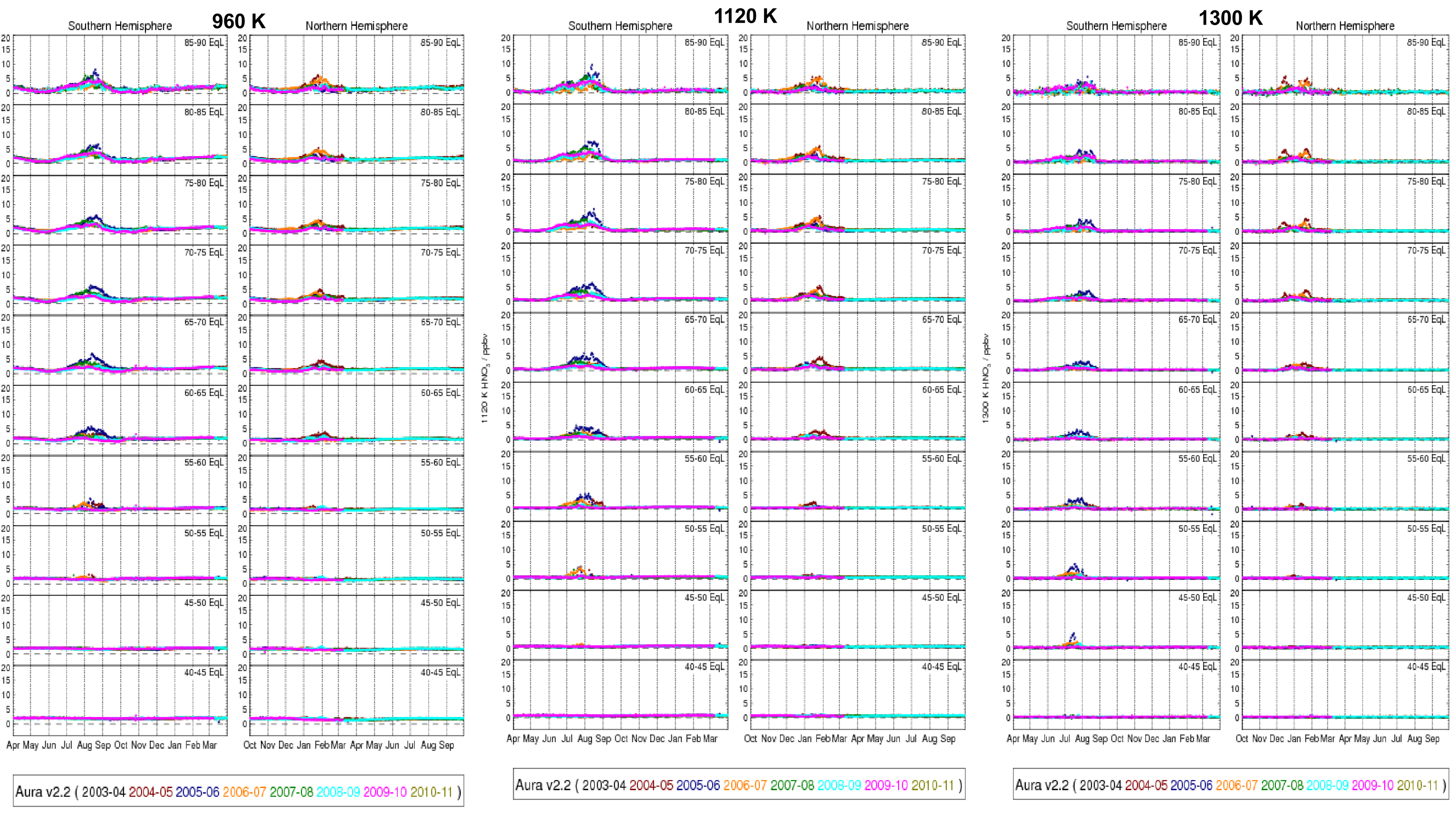
This study examines nitric acid (HNO_3) and several other reactive nitrogen species and their interactions from 25-45 km at high latitudes. Utilizing data from the EOS-Aura Microwave Limb Sounder (Aura-MLS) and the Atmospheric Chemistry Experiment's Fourier Transform Spectrometer (ACE-FTS) satellite instruments, we investigate the enhancement in HNO_3 above the primary peak. We first analyze the production and loss cycle of HNO_3 using HNO_3 and hydroxyl (OH) from Aura-MLS and a calculated daily average of nitrogen dioxide (NO_2) from ACE-FTS. We then examine the transport and dynamical effects to better understand their role in the enhancement in HNO_3 above its primary maximum.

What enhancement?



Above: Equivalent latitude theta time series of HNO_3 for three different theta levels (960 K, 1120 K, and 1300 K respectively) for both the northern and southern hemispheres. Notice the enhancement (during polar winter) in HNO_3 in all latitude bins poleward of 60 degrees. Correlations between seasonal variation, geomagnetic activity, solar cycle, and strong stratospheric warming (SSW) effects and the enhancements (not shown here) are not significant therefore indicating other processes account for the enhancements.

Can an analysis of chemical production and loss explain, even in part, the enhancement in HNO_3?

Primary production process for HNO_3:

$NO_2 + OH + M \rightarrow HNO_3 + M$ (1)

Primary loss process for HNO_3:

$HNO_3 + h\nu \rightarrow OH + NO_2$ (2)

$HNO_3 + OH \rightarrow NO_3 + H_2O$ (3)

Therefore the continuity equation is as follows:

$$d([HNO_3])/dt = k_1[NO_2][OH] - (J_{HNO3}[HNO_3] + k_3[HNO_3][OH])$$

All values are given as daily averages

k_1	: Reaction rate for (1)	- taken from JPL '06
J_{HNO3}	: Photolysis frequency for (2)	- Radiation calculation
k_3	: Reaction rate for (3)	- taken from JPL '06
[OH]	: Aura-MLS v2	- Very strong diurnal variation
$[HNO_3]$	: Aura-MLS v2	- No significant diurnal variation
$[NO_2]$	: ACE-FTS v2	- Very strong diurnal variation

Aura-MLS does not measure NO_2, so and we use NO_2 from ACE-FTS. Incorporating ACE-FTS NO_2 into this calculation was a challenge given that ACE-FTS is a solar occultation experiment (with at most 15 measurement points per day at each of two seasonally varying latitudes). Here we have developed a technique to calculate the diurnal average of ACE-FTS NO_2 and perform a comparison to daily NO_2 profiles calculated by a full photochemical box model developed by McLinden et al. as a validation check.

Using diurnal profiles calculated by Ko and Sze (1984) & Logan et al. (1978) for NO, NO_2, N_2O_5 and the sum of these three species to be fairly constant throughout the region of interest, we developed the following:

$$NO_2^{avg}=(DLH/24.)*(R_{day})*\Sigma_N^{measured} + (1-(DLH/24.))*(R_{night})*\Sigma_N^{measured}$$

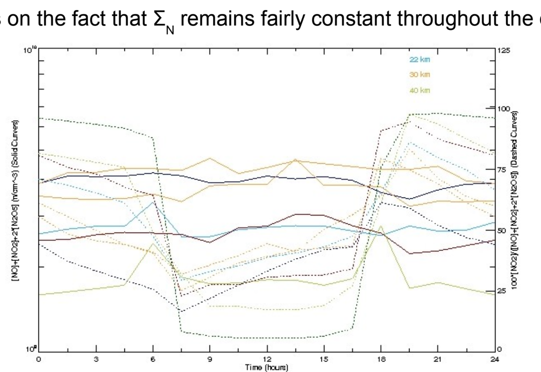
DLH – Number of daylight hours

R_{day} – Ratio of day time NO_2^{model} to Σ_n^{model}

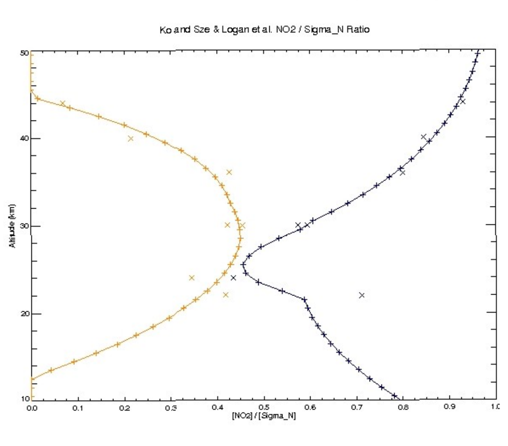
R_{night} – Ratio of night time NO_2^{model} to Σ_n^{model}

Σ_N - Sum of NO, NO_2 and $2*N_2O_5$

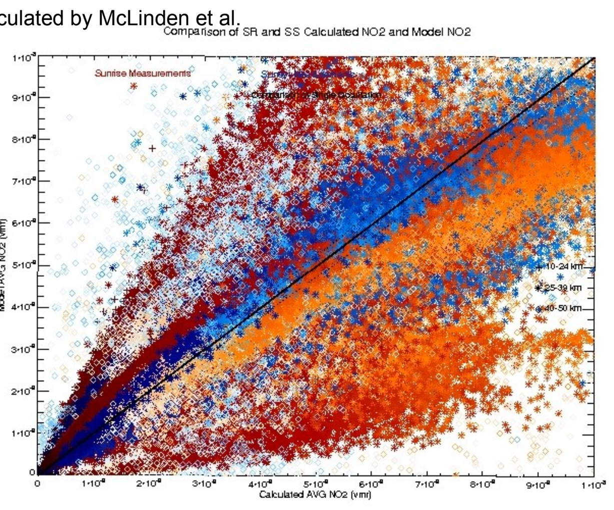
This relies on the fact that Σ_N remains fairly constant throughout the day as seen here:



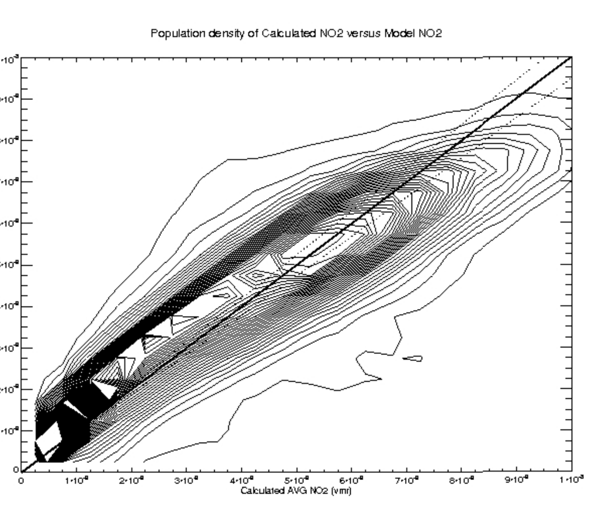
This then allowed us to produce a profile of R_{day} and R_{night} by the following:



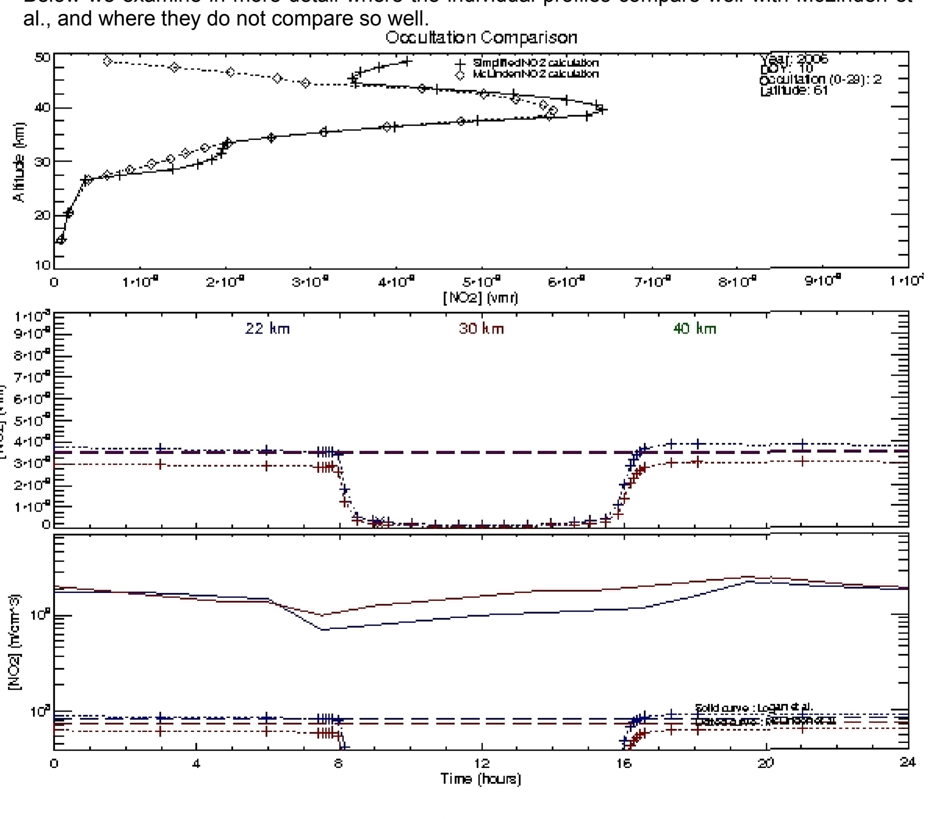
Now that we have a a value for average NO_2, we need to compare it against another calculation. Here we are comparing with an average NO_2 calculated by McLinden et al.

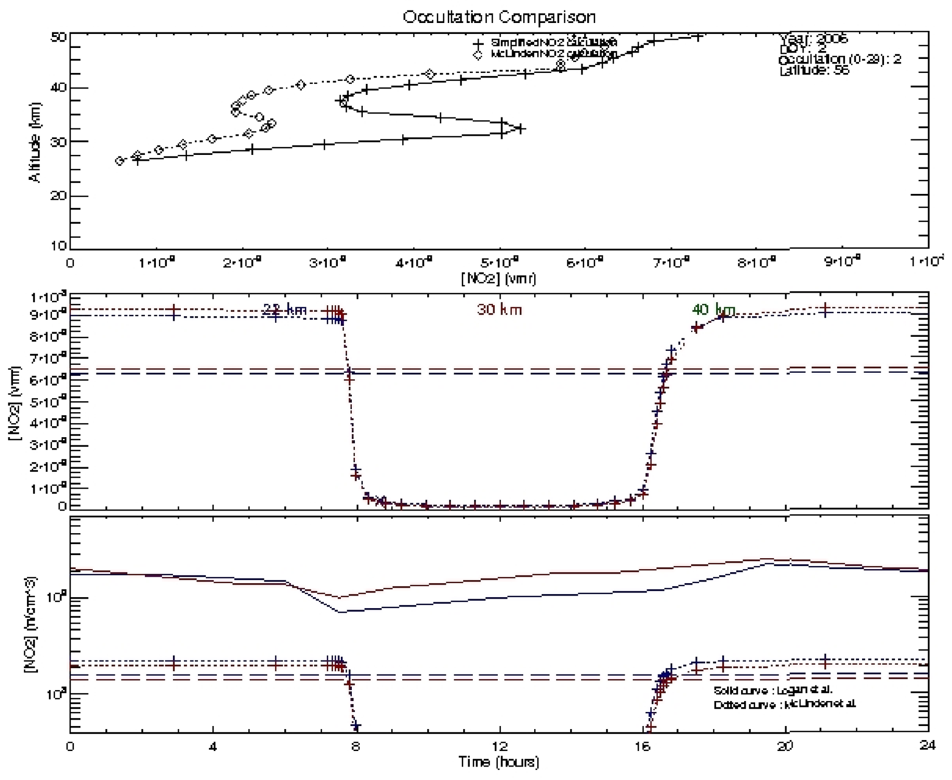


Obviously there is some deviation from the 1:1 but this is reasonable. The real question is how much deviation there is. If we look at a density plot of this comparison we see that in fact it compares very well overall.



Below we examine in more detail where the individual profiles compare well with McLinden et al., and where they do not compare so well.





In the above two figures, the top panel shows the vertical profile of both our calculated NO_2 and the NO_2 calculated by McLinden et al. The middle and bottom panels examine the dirunal profile NO_2 at three different altitudes (22 km, 30 km, and 40 km). The dashed curve is our calculated average value at these heights. The 'X' represents the measured ACE-FTS NO_2 recorded. The dotted curve is the diurnal profile calculated by McLinden et al. The bottom panel compares diurnal profiles from McLinden et al. and Logan et al. In the first panel of the top figure, we see an overall very good comparison between the two vertical profiles. Only at the uppermost altitudes do the two profiles diverge. This is to be expected because we assume that the relationship between NO, NO_2, and N_2O_5 only holds to ~45km. If we now examine the top panel on the bottom figure, we see greater disagreement between the two vertical profiles between 30-40 km. We believe this discrepancy is due to large quantities of NO in the altitude region and the dependance of NO_2 on NO from the NO_x relationship. The important thing to note on the bottom figure is that the characteristics of the vertical profile are the same.

It is important to note that the McLinden et al. do not calculate NO_2 directly. Instead they calculated the diurnal profile from their box model and then their data must be scaled to match the values measured by ACE-FTS. More information on how McLinden et al. can be found in the following:

McLinden, C. A., et al., Stratospheric ozone in 3-D models: A simple chemistry and the cross-tropopause flux, J. Geophys. Res., 105, 14653-14665, 2000.

Prather, M. J., Catastrophic loss of stratospheric ozone in dense volcanic clouds, J. Geophys. Res., 97, 10,187-10,191, 1992.

We can now move on to calculate a daily average OH. Calculating the daily average OH is not easy because of the Aura satellite's sun synchronous orbit. To calculate the daily average OH, we use a method developed by Minschwaner et al. (2010), and calculate the OH through the following:

$$[OH](t)=[OH]_0\exp(-0.5*tau_{O3}\sec[\theta(t-\Phi)])$$

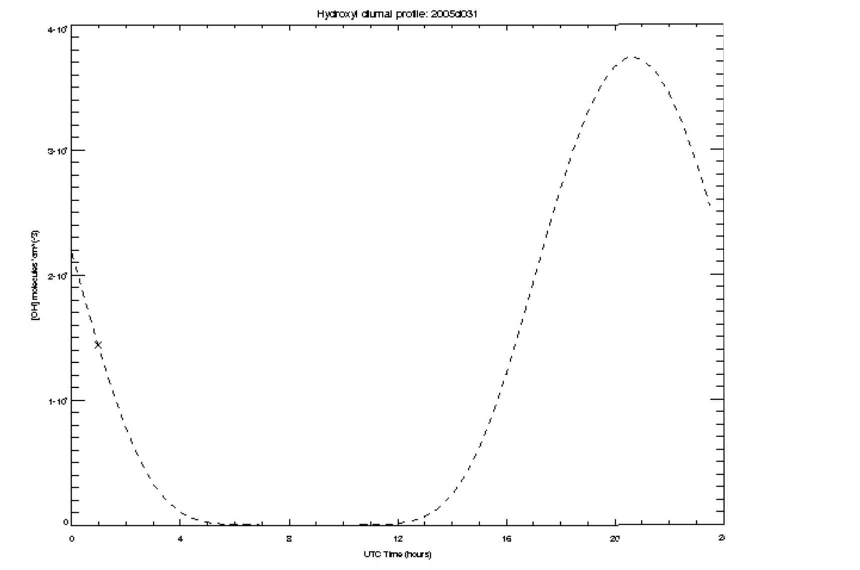
[OH](t) : OH concentration given at any time

$[OH]_0$: OH diurnal maximum

Tau_{O3} : Ozone vertical optical depth

Θ : Solar zenith angle at given time t with a phase lag given by Φ

Φ is set to ½ hour to account for the approximate time constant due to HO_x photochemistry.



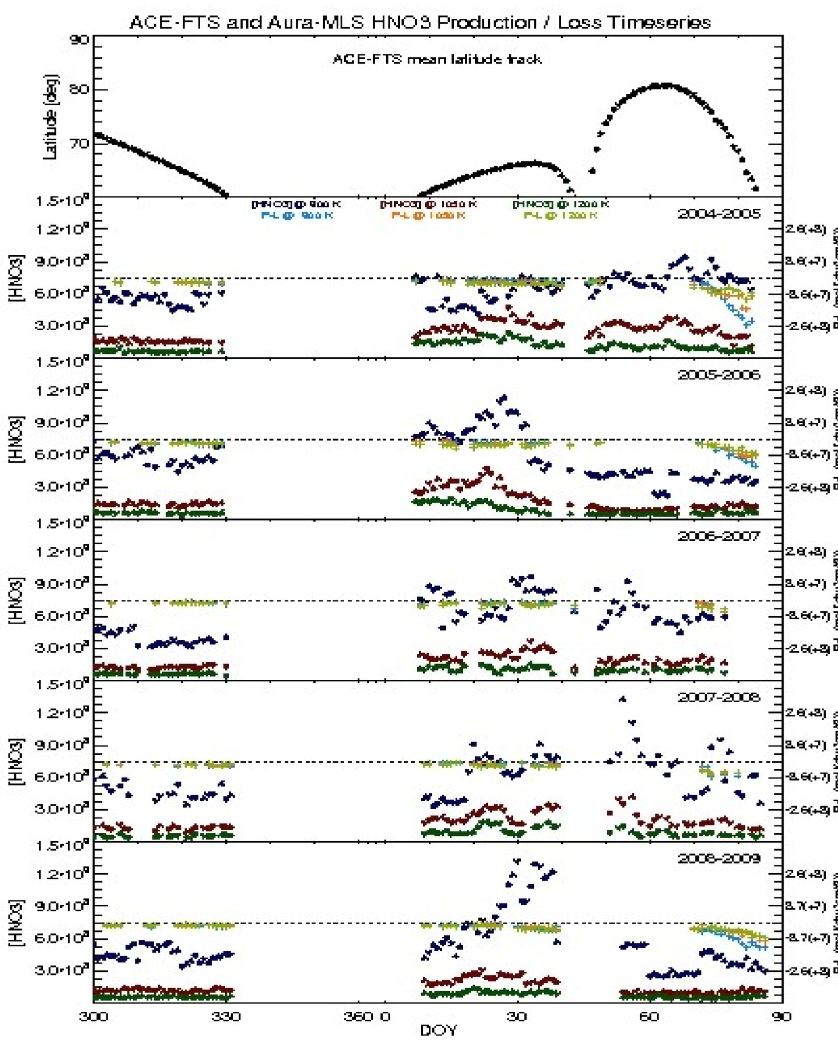
It is important to note that this method is only appropriate for solar zenith angles less than ~70° due to the plane-parallel assumption. An example diurnal profile of OH is seen to the right, where the 'X' marks the measured OH from Aura-MLS. The curve is not centered around noon because this profile is set at local time while the x-axis is UTC time.

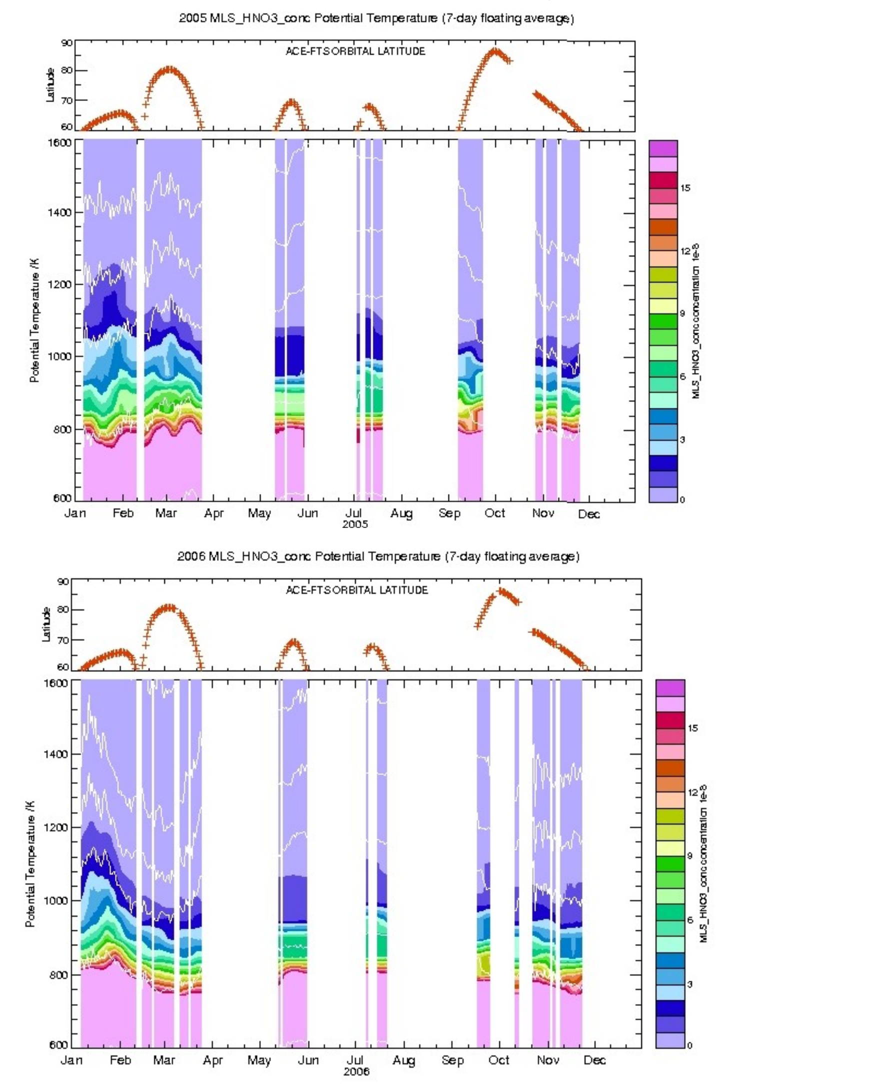
For more information on this technique, please refer to:

Minschwaner, K., et al. (2010), The photochemistry of carbon monoxide in the stratosphere and mesosphere evaluated from observations by the Microwave Limb Sounder on the Aura satellite, J. Geophys. Res., 115, doi:10.1029/2009JD012654.

Now that we are confident in our calculation of a daily average NO_2 and OH, we can now calculate HNO_3 chemical production and loss and see what effect it may play in the high altitude enhancement.

Taking zonally averaged NO_2 from ACE-FTS, HNO_3 and OH from Aura-MLS, matching all of the data sources to within 2.5 degree latitude we can now apply our chemical production and loss formula. Below (left) we see a time series of HNO_3 & production and loss at 3 different potential temperature levels (900 K, 1050 K, and 1200 K). Below (right) we see a time series of HNO_3 on a potential temperature grid where general pressure lines are over plotted.

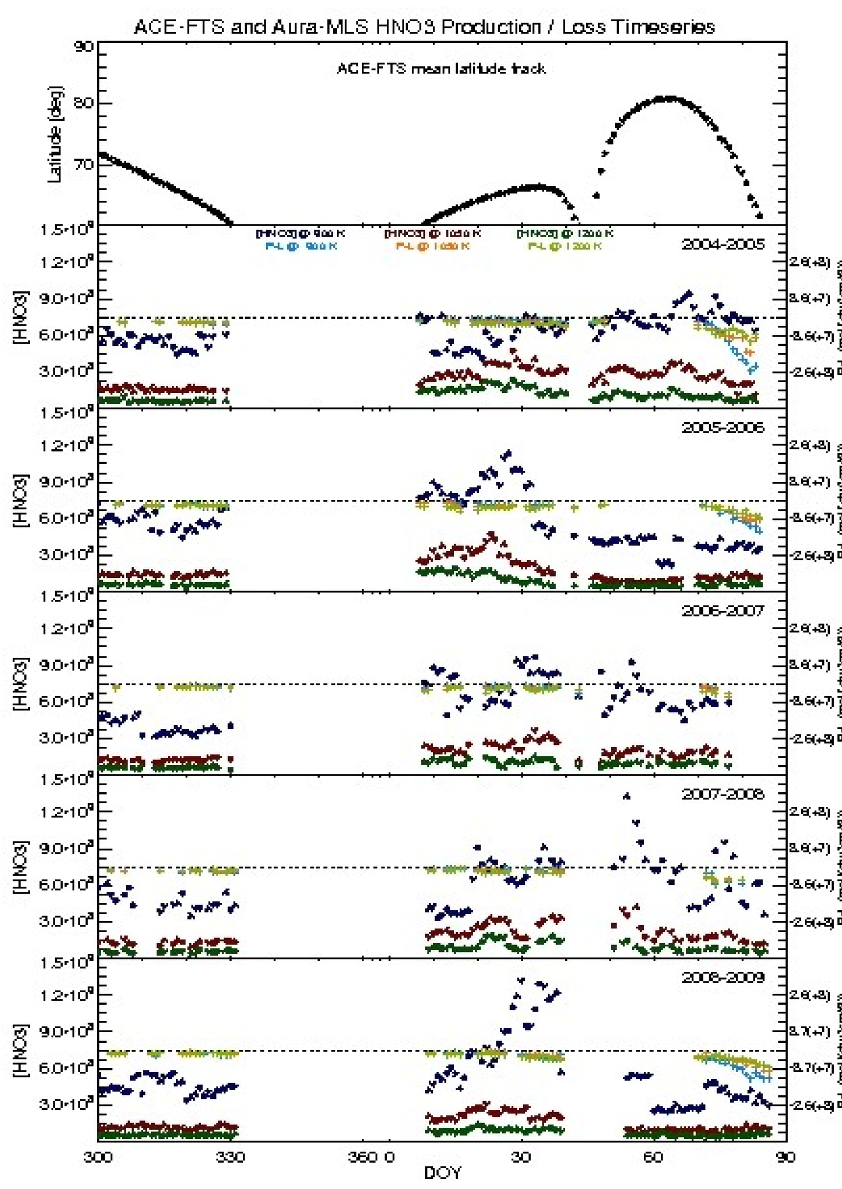


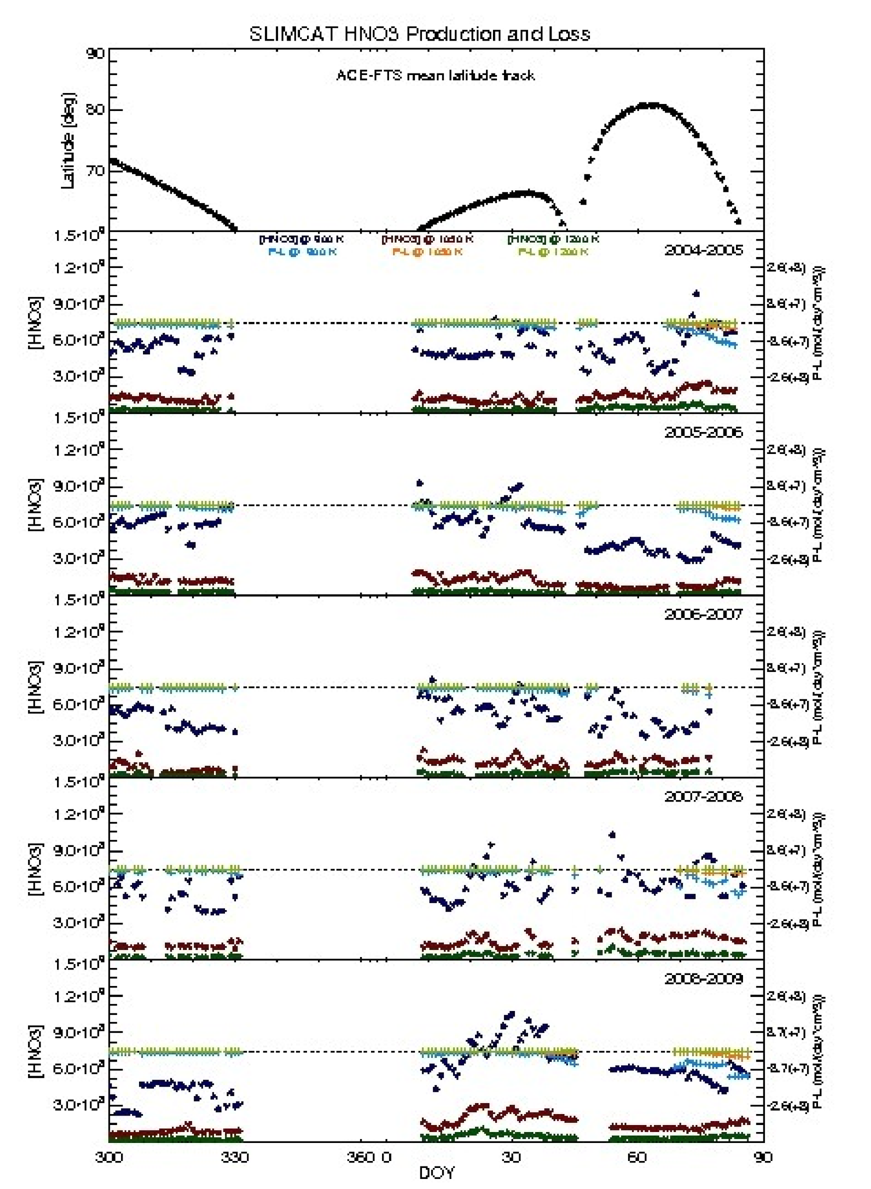


Above (left): As we examine the HNO_3 curves around day 30 we do in fact see an increase in the HNO_3 concentration in every year which is consistent with plots shown earlier, but when we look at the production and loss curve, we notice rates are very small. We believe this is mainly due to the absence of sunlight and hence low OH reacting with NO_2 to produce HNO_3.

Above (right): HNO_3 time series plotted on a potential temperature grid for the northern hemisphere with approximate pressure values over plotted. Here is is important to note the advantages of looking on a constant potential temperature grid rather than a constant pressure grid. In years of strong warming during the winter (e.g. 2006), the pressure grid can vary greatly when compared to the potential temperature grid and hence one might miss the HNO_3 enhancement altogether if focusing on a single pressure level.

We also compare our chemical production and loss to a calculated production and loss using SLIMCAT model simulations sampled in the same manner as the MLS data.

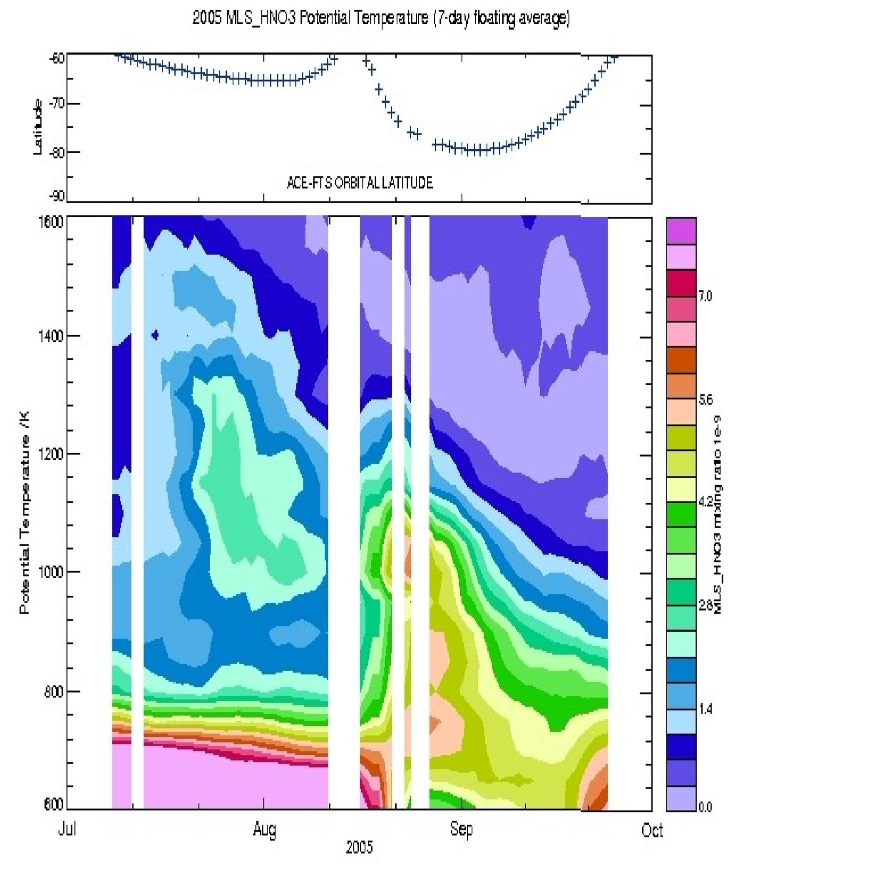




Above we have a side by side of the ACE-FTS / Aura-MLS HNO_3 chemical production & loss plot and the SLIMCAT production & loss plot. At first glance, one will note how similar the two plots look. Upon closer inspection we see that the Aura-MLS HNO_3 is greater at all three levels shown when compared to the values calculated by SLIMCAT. The magnitude of the production and loss values for SLIMCAT are also smaller than those calculated by using ACE-FTS and Aura-MLS data. Also note that SLIMCAT does not show any sign of significantly enhanced production during the enhancements.

Summary:

- We have developed a method for calculating an average daily NO_2 that is both computationally simple and compares well with a computationally intensive box model calculation
- The standard chemical production and loss cycle of HNO_3 as described by Brasseur and Solomon (1986) cannot account for a significant portion of the enhancement in HNO_3 seen every year to varying degrees
- As seen to the right, transport of HNO_3 does exist but it does not suggest the origin of the enhancement itself
- We have compared method of measured production and loss to the calculated values from SLIMCAT and found that overall, SLIMCAT misses the enhancement in HNO_3
- We have applied our method for calculating production and loss from observations to SLIMCAT model simulations, and found that SLIMCAT also does not show enhanced production, and in fact does not simulate the enhancements well
- Because the SLIMCAT model simulations have a standard chemistry package, and dynamics from the ECMWF driving winds / temperature (though these become less reliable in the upper stratosphere), we believe that the enhancement in HNO_3 may be due to ion chemistry which is not included in our calculations or through indirect effects of auroral activity.



Outlook:

- We plan to examine the chemical production and loss cycle with NO_2 calculated from McLiden et al. and compare it with our own
- We will take a more in-depth look at transport and dynamics to try and figure out exactly how much of a role they play by examining observed and modeled (SLIMCAT) log-lived tracers such as CH_4 and CO.